5 DISCUSSION

5.1. Characteristics of carbons

Examination of carbon characteristics (Table 3) shows that both the carbons possess similar bulk densities. High moisture content of PHC is evidently due to low temperature carbonisation using sulphuric acid. The method of preparation aids the introduction of ion exchange groups and removal of certain inorganics as soluble salts as is apparent from the data on ion exchange capacity and ash content of the carbons. Higher decolourizing power and lower phenol number of GAC imply that it is also suitable for organic adsorption. The surface area of activated carbons prepared from agricultural by-products such as almond shells, olive stones and peach stones, respectively, has been reported to be 1103, 1316 and 876 m$^2$/g [221]. The higher surface area of the above carbons was due to high temperature carbonization processes. The surface area of low temperature carbons prepared from rice husk [162] and coconut shell [164] has been reported to be 378 and 168.6 m$^2$/g, respectively. These values are comparable with those of PHC. Commercial carbons have a typical surface area range of about 400 to 1600 m$^2$/g [101]. The pH$_{ZPC}$ values (Fig. 1) of PHC (4.7) and GAC (7.2) are comparable with those of Nuchar C-190-N and Filtrasorb 400, respectively. The pH$_{ZPC}$ values for various activated carbons such as Nuchar C-190-N, Nuchar 722, Darco, Pittsburgh (PAC) and Filtrasorb 400 have been reported to be 4.75, 5.70, 6.15, 6.70 and 7.10, respectively [20].

5.2 Batch mode studies

Systematic laboratory batch mode studies were carried out with PHC and GAC to evaluate the optimum conditions for the removal and recovery of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) and to assess their potentiality for treatment of water and wastewater containing these metal ions. In this study a good contact was made between the adsorbent and adsorbate by agitating at 180 rpm. The parameters which influence the extent of adsorption such as metal ion concentration, agitation time, adsorbent concentration and pH were investigated. In addition to the above parameters, the desorption of metals from the metal-laden carbons was studied. In order to testify the results
obtained from the batch mode studies, industrial wastewaters containing the metals were subjected to treatment using both carbons.

5.2.1 Effect of agitation time and metal ion concentration on metal adsorption

Figures 2-6 show that increasing contact time increased the metal uptake for all the metals studied and it remained constant after the equilibrium time for both carbons. It is clear from Table 14 that the contact time required for maximum removal of metal by PHC would be 1.6-5.0 times less than that required by GAC for the metal ions studied. The equilibrium time was independent of initial metal ion concentrations for all the metal ions studied. It could be seen that increase in initial metal ion concentration increased the amount of metal uptake per unit weight of the adsorbent (mg/g) for both carbons (Tables 4-13 and Figs.2-6). Similar results have been reported by several authors for metal adsorption [42, 97, 98, 108, 114, 222-224]. The metal uptake (q) vs time curves were single, smooth and continuous leading to saturation, suggesting possible monolayer coverage of metal ions on the surface of the adsorbents [123, 204].

5.2.2 Adsorption kinetics

The kinetics of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) adsorption follow the first order rate expression given by Lagergren [121].

\[
\log_{10}(q_e - q) = \log_{10} q_e - k_{ad} t/2.303
\]

where \( q \) and \( q_e \) are the amounts of metal ion adsorbed, mg per g of adsorbent at time, \( t \) (min) and at equilibrium time, respectively, and \( k_{ad} \) is the rate constant of adsorption (1/min). The linear plots of \( \log_{10}(q_e - q) \) vs \( t \) for all the metals studied at different concentrations show the applicability of the above equation for both PHC and GAC (Figs.7-11). The \( k_{ad} \) values were calculated from the slopes of the linear plots and are presented in Table 35 for different concentrations of metal ions. The metal concentration, generally, did not have any significant effect on the rate constant of adsorption. However, it could be observed that the adsorption rate constants for all the metal ions studied were lower for GAC compared to PHC. The values of rate constant are comparable with those in
literature for both carbons. Adsorption of Cr(VI) on feldspar [204] and fly ash - Wollastonite [114] obeyed the Lagergren equation and \( k_{ad} \) values were found to be \( 2.994 \times 10^{-2} \, \text{1/min} \) and \( 3.1 \times 10^{-2} \, \text{1/min} \) at 30°C, respectively. Arulanantham et al. [164] have found that the adsorption rate constant for coconut shell carbon for Cd(II) and Pb(II) decreased with increase in concentration. The rate constant for the adsorption of Ni(II) on fly ash was reported to be \( 2.303 \times 10^{-2} \, \text{1/min} \) at 30°C and pH 3.5 [108]. According to literature, the rate constant for the adsorption of Cr(VI) by waste tea, turkish coffee, exhausted coffee, nut shell, walnut shell [129], activated groundnut husk carbon [163] and coconut shell carbon [225] were reported to be \( 1.516 \times 10^{-1}, 1.738 \times 10^{-1}, 1.585 \times 10^{-1}, 1.549 \times 10^{-1}, 1.349 \times 10^{-1}, 3.455 \times 10^{-1} \) and \( 9.4 \times 10^{-2} \, \text{1/min} \), respectively.

5.2.3 Effect of carbon concentration on metal adsorption

The percent removal of metal ions increased with the increase in adsorbent concentration and reached a constant value after a particular adsorbent concentration for all the metal ions studied for both carbons (Figs.12-16). This is obvious because a larger mass of adsorbent can adsorb larger amount of metal ion due to the availability of more surface area of the adsorbent. But for each metal ion studied, the amount of metal ion adsorbed after equilibrium per unit weight of adsorbent \( (q_e) \) is different. It could be seen from the figures that for the maximum removal of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) from a 100 mL solution containing 20 mg/L, a minimum PHC concentration of 0.7, 0.3, 0.7, 0.9 and 0.9 g/L or GAC concentration of 5.0, 3.5, 12.5, 12.0 and 13.0 g/L, respectively, is required. The percent removal of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) from a 100 mL solution containing 20 mg/L was quantitative for PHC. However, the corresponding values for GAC were 99.3, 92.4, 90.6, 35.0 and 95.0. In the case of GAC, increasing the adsorbent concentration increased the metal uptake upto a certain level and afterwards the uptake reached a plateau. Quantitative removal of Pb(II), Cd(II), Ni(II) and Cu(II) by GAC was not observed except for Hg(II).
5.2.4 Adsorption isotherms

Adsorption data for wide ranges of adsorbate concentrations are most conveniently described by adsorption isotherms, which relate adsorption density, \( q_e \) (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, \( C_e \).

The Langmuir isotherm treats surface sites analogous to dissolved complexing ligands and it is based on the assumptions that maximum adsorption corresponds to a saturated monolayer of adsorbate molecules on the adsorbent surface, that the energy of adsorption is constant and that there is no transmigration of adsorbate in the plane of the surface. The Langmuir isotherm is represented by the following equation [226],

\[
\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0}
\]

where \( C_e \) is the equilibrium concentration (mg adsorbate/litre of solution) and \( q_e \) is the amount adsorbed (mg/g of adsorbent) at equilibrium and \( Q_0 \) and \( b \) are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The plots of \( C_e/q_e \) vs \( C_e \) are linear for both carbons which show that the adsorption follows the Langmuir isotherm model for the metals Hg(II) (Fig. 17), Pb(II) (Fig. 18), Cd(II) (Fig. 19), Ni(II) (Fig. 20) and Cu(II) (Fig. 21). The values of \( Q_0 \) and \( b \), respectively, were determined from the slope and intercept of the respective plots for both carbons and are presented in Table 36. The \( Q_0 \) values decreased in the order: Pb(II) > Hg(II) > Cd(II) > Cu(II) > Ni(II) for PHC and Hg(II) > Pb(II) > Cu(II) > Cd(II) > Ni(II) for GAC. The \( Q_0 \) values for the adsorption of Pb(II), Ni(II) and Cd(II), respectively, have been reported by Larsen and Schierup [147] as 15.2, 6.4 and 7.7 mg/g for straw (untreated), 14.1, 4.6 and 6.6 mg/g for straw (washed), 5.0, 1.3 and 1.8 mg/g for saw dust and 19.5, 8.1 and 11.1 mg/g for activated carbon. Recently, Namasivayam and Ranganathan have reported the \( Q_0 \) values for the adsorption of Pb(II) [123], Ni(II) [125] and Cd(II) [124] by waste Fe(III)/Cr(III) hydroxide as 126.58, 21.00 and 40.49, respectively. For the adsorption of Cu(II) and Pb(II) onto palm fibre, the \( Q_0 \) values were found to be 16.7 and 24.0 mg/g, respectively, and onto coconut husk, 35.0 and 33.3 mg/g, respectively [146]. Srivastava et al. [165] have reported that the \( Q_0 \) values at 27°C for the adsorption of Cr(VI) and Pb(II) by carbonaceous materials developed from fertilizer plant waste slurry were 371.3 and
In the case of GAC, the $Q_0$ values are comparable with literature data. The ratio of $Q_0$ values of PHC and GAC was 8.88, 18.23, 32.54, 36.00 and 18.21 for Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II), respectively, indicating that the capacity of PHC is superior to GAC for all the metal ions studied.

The essential characteristics of Langmuir isotherm can be expressed in terms of dimensionless constant separation factor or equilibrium parameter, $R_L$ [227] which is defined by,

$$R_L = 1/(1 + b C_0)$$

where $C_0$ is the initial metal ion concentration (mg/L) and $b$ is the Langmuir constant (L/mg). The parameter indicates the shape of isotherm as follows:

<table>
<thead>
<tr>
<th>$R_L$</th>
<th>Type of isotherm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_L &gt; 1$</td>
<td>Unfavourable</td>
</tr>
<tr>
<td>$R_L = 1$</td>
<td>Linear</td>
</tr>
<tr>
<td>$0 &lt; R_L &lt; 1$</td>
<td>Favourable</td>
</tr>
<tr>
<td>$R_L = 0$</td>
<td>Irreversible</td>
</tr>
</tbody>
</table>

For both PHC and GAC, $R_L$ values were found to be between zero and one (Table 37) at all the concentrations of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) studied, indicating favourable adsorption.

The Freundlich equation is basically empirical, but is often useful as a means of data description. The Freundlich equation can be derived by assuming that the free energy of adsorption decreases logarithmically as adsorption density increases. The equation is used for heterogeneous surface energies in which the energy term, $Q_0$ in the Langmuir equation varies as a function of the surface coverage, $q_e$, strictly due to variations in the heat of adsorption [228]. The Freundlich adsorption isotherm was also applied for the adsorption of metal ions by both PHC and GAC. The Freundlich constants $k_f$ and $n$ were calculated from the following equation [229].
where $q_e$ is the amount adsorbed mg per g of adsorbent used. The value of $n$ gives an indication of the favourability and $k_f [(mg/g)/(L/mg)^n]$, the capacity of the adsorbent. Linear plots of $\log_{10} q_e$ vs $\log_{10} C_e$ show that the adsorption of metal ions onto both PHC and GAC also follows Freundlich isotherm model (Figs.22-26) indicating that the average energy of adsorption decreases with increasing adsorption density. These results may be explained if adsorbent surfaces have several different types of sites [230]. The values of $n$ and $k_f$ were calculated from the slope and intercept of the plots and are presented in Table 38 for both PHC and GAC. The values of $k_f$ decreased in the order: Pb(II) > Cd(II) > Hg(II) > Ni(II) > Cu(II) for PHC and Hg(II) > Pb(II) > Cu(II) > Cd(II) > Ni(II) for GAC. Srinivasan [231 has reported that the $k_f$ and $n$ values for the adsorption of Hg(II), Pb(II) and Cd(II) onto bicarbonate treated rice husk were $(k_f) 5.84, 25.11$ and $31.62$ and $(n) 2.00, 5.88$ and $5.00$, respectively. Soldatini et al. [190] have found that the $k_f$ and $n$ values for the adsorption of Pb(II) on different soil samples varied from 3.9 to 41.7 and 5.0 to 11.1, respectively. For Cd(II) adsorption on Danish soil sandy loam, the values of $k_f$ and $n$ were reported to be 0.386 and 1.2, respectively [232]. Mirgaya and Page [187] have found that the adsorption of Cd(II) by soils with different chemical and mineralogical composition conformed well with the Freundlich adsorption isotherm; $k_f$ varied from 10.5 to 87.1 and $n$ from 1.05 to 1.59. According to McKay et al. [228], the values of $n$ between 1 and 10 (Table 38) represent good adsorption of metal ions onto both PHC and GAC.

5.2.5 Effects of pH on metal ions removal

Figures 27 and 28, 29 and 30, 31 and 32, 33 and 34, 35 and 36, respectively, show the effect of pH on the adsorption of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) onto PHC and GAC. The percent removal of metal ion increased with increase in pH for all the metal cations, which is typical of cation adsorption by metal oxides/hydroxides [108, 123-125, 224]. For comparison, curves for precipitation by hydrolysis at different pH values for all metal ions except Hg(II) in the absence of carbons are also shown in the respective figures. A decrease in the concentration of metal ion in
solution occurred by hydrolysis after pH 6.2, 8.3, 7.7 and 5.5 for Pb(II), Cd(II), Ni(II) and Cu(II), respectively. This suggests that the respective cations are precipitating from solution at these pH values for a particular concentration. However, in the presence of adsorbents, the removal started at much earlier pH values. Figures clearly show that at any pH value, the efficiency of metal removal is greater by adsorption in the presence of adsorbents than by precipitation by hydrolysis in the absence of adsorbents. In the case of Hg(II), increase in pH in the absence of adsorbent did not remove the metal ion by hydrolysis owing to the formation of chloro complexes of Hg(II): HgCl+, HgCl₂, HgCl₃⁻ and HgCl₄²⁻ [233]. The chloride ion effectively reduces the degree of hydrolysis of the mercuric ion by blocking some of the co-ordination positions. From these reactions it is possible to generate three uncharged species HgCl₂, HgClOH and Hg(OH)₂ all of which are linear and all probably exist in natural water systems. Adsorption of metal cation on the adsorbent depends upon the nature of adsorbent surface and species distribution of the metal. Species distribution depends mainly on the pH of the system. The main metal species for Pb, Cd, Ni and Cu present in the pH range studied are M²⁺ and M(OH)⁺ [195, 234-237]. In the case of Hg, species such as HgCl₂, HgCl⁺, Hg²⁺, HgOH⁺, HgOHCl and Hg(OH)₂ are present in the pH range studied [196].

Figures 27 and 28 show that PHC is effective for the removal of Hg(II) over the pH range 3.5 to 10.0. GAC, however, is effective within a narrow pH range, 3.5 to 5.0. It can be shown by stability constant calculations that in the presence of Cl⁻, the predominant species for Hg(II) at pH > 4.0 is Hg(OH)₂ and at pH < 4.0 is HgCl₂ [196]. It was reported that the formation of HgCl₂ decreased the Hg(II) sorption onto a commercial FS-400 GAC [97]. Accordingly, the Hg(II) sorption decreased when the pH was lowered from 4.0 to 2.0 with hydrochloric acid for both PHC and GAC. Increase of pH above 4.0 shows no change in the uptake of Hg(II) by PHC. On the contrary, increase of pH above 4.0 decreased the percent adsorption by GAC probably because of the formation of soluble hydroxide complexes of mercury, Hg(OH)₂ (aq). This is in agreement with the studies by Humenick and Schnoor [95] and Ma et al. [97] on the effect of pH on mercury sorption by activated carbons by FS-300 and FS-400, respectively. These results imply that a third process may be involved, namely, retention of the Hg(OH)₂ species in the micropores of the PHC particles.
Chemisorption and/or precipitation of a new phase may be the dominant process in PHC with surface complex dissociation equilibria.

For other metal ions, Pb(II), Cd(II), Ni(II) and Cu(II) a maximum removal by both carbons was observed over the pH range 4.0-10.0 (Fig.29-36). The influence of pH on metal ion removal may probably be explained as follows: Significant adsorption is observed below pH 3.0. At the same time both adsorbent (pHzpc = 4.7 for PHC and 7.2 for GAC) and adsorbate species are positively charged and therefore the interaction is that of electrostatic repulsion. Besides this, a higher concentration of H+ ions present in the reaction mixture competes with the positively charged metal ions for the adsorption sites, resulting in the reduced uptake of metal ions. As the pH increases, the concentration of H+ ion decreases, whereas the concentration of metal ions (M2+) remain constant and therefore the uptake of metal ions can be explained as an H+·M2+ exchange reaction. Similar results of pH effect were reported for the adsorption of Pb(II), Cd(II) and Cu(II) onto Fe(OH)3 and FeOOH [179], goethite [174], hydrous iron oxides [238] and on amorphous iron oxyhydroxide [230].

Adsorption of Cd(II) and Pb(II) by coconut shell carbon [164] and Cd(II) by coconut shell and rice husk [239] also followed the same trend. Adsorption of Ni(II) was high at higher pH values for hydrous oxide gels of iron [240] and FeOOH [241]. Data in literature and in the present work show that appreciable adsorption of metal cations occurred at pH values below pHzpc of the adsorbent, though the adsorbent surfaces were mostly positively charged. Since the electrostatic attraction was not possible between positively charged adsorbent and positively charged metal ion species, it appears that some non-electrostatic forces and specific chemical interaction were involved in the adsorption processes. Further discussion on the mechanism of adsorption is deferred to section 5.4.

5.2.6 Desorption studies

Desorption studies help elucidate the mechanism of adsorption and recover precious metals from wastewaters and the adsorbents. A maximum Hg(II) recovery of 47.0 and 12.6% from spent PHC and GAC, respectively, was achieved with 0.60 M hydrochloric acid (Fig.47). In order to improve the percent recovery, attempts were then made to desorb Hg(II) using potassium iodide.
solution of various strengths. With 1.0% potassium iodide solution, the recovery of Hg(II) obtained was 87.0 and 23.6% for PHC and GAC, respectively (Fig.48). Higher desorption of Hg(II) by I⁻ might be due to the formation of relatively more stable iodide complexes compared to chloride complexes [242]. Quantitative recovery of Pb(II), Cd(II) and Ni(II) was obtained from the spent carbons with 0.10, 0.05 and 0.15 M hydrochloric acid, respectively for both PHC and GAC (Figs.49-51). Quantitative recovery of Cu(II) was observed with 0.05M hydrochloric acid for PHC and with 0.10 M hydrochloric acid for GAC (Fig.52). In acidic conditions, H⁺ ions protonate the adsorbent surface by replacing the metal ion species, M²⁺ and/or MOH⁺, indicating that ion exchange mechanism is involved in the adsorption processes.

5.2.7 Tests with industrial wastewaters for the removal of metal ions using PHC and GAC

The removal of heavy metals from industrial wastewaters depends upon the composition and pH. Table 30 shows that the chloralkali industry wastewater was slightly alkaline and contained large amounts of total solids, sodium and chloride contents. Table 31 shows that radiator manufacturing industry wastewater was highly acidic and the total solids, hardness and chloride contents were very high. Table 32 presents the composition of synthetic wastewater containing Cd(II). Table 33 shows that nickel plating industry wastewater was highly acidic and almost clear. It contained large amounts of total solids and a high concentration of iron, nickel (II) and sulphate. Table 34 shows that the copper plating industry wastewater was also acidic and contained a fairly large amount of total solids.

Effects of pH

Figure 53 shows that the per cent removal of Hg(II) from chloralkali industry wastewater increased with pH and reached a maximum of 91.3% by PHC at pH 9.0 and 63.0% by GAC at pH 8.0. Figure 54 shows that the removal of Pb(II) from radiator manufacturing industry wastewater attained a maximum of 92.5% and 85.6% by PHC and GAC, respectively, over the pH range of 4.0 to 10.0. Figure 55 shows that for the maximum removal of Cd(II) (100% by PHC and 54.6% by GAC) from synthetic wastewater, the effective pH range was 4.0 to 10.0 and 5.0 to 10.0 for the PHC and
GAC, respectively. It is clear from Fig. 56 that for the maximum Ni(II) removal of 71.2% by PHC and 64.0% by GAC from nickel plating industry wastewater, the effective pH range was 3.5 to 10.0 and 5.0 to 10.0 by PHC and GAC, respectively. Figure 57 shows that for the maximum Cu(II) removal of 50.3% by PHC and 20.7% by GAC from copper plating industry wastewater, the effective pH range was 4.0 to 10.0 for both carbons.

Effects of carbon concentration

Figures 58-62, respectively, show that increasing carbon concentration increased the percent adsorption for Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) from industrial wastewaters. It could be seen from the figures that for the quantitative removal of Hg(II) (20 mg/L), Pb(II) (19.68 mg/L), Cd(II) (20 mg/L), Ni(II) (125 mg/L) and Cu(II) (19.60 mg/L), the minimum concentration of PHC required was 1.6, 0.5, 1.0, 7.0 and 1.7 g/L, respectively. However in the case of GAC, a maximum removal of 100, 91, 78, 84 and 43%, respectively, was obtained for Hg(II) (20 mg/L), Pb(II) (19.68 mg/L), Cd(II) (20 mg/L), Ni(II) (12.5 mg/L) and Cu(II) (19.60 mg/L). The minimum concentration of GAC required was 15.0, 4.5, 17.0, 13.0 and 15.0 g/L, respectively. Quantitative removal of Pb(II), Cd(II), Ni(II) and Cu(II) by GAC could not be observed even with the higher concentration of GAC. This is similar to the adsorption of metal ions by GAC in aqueous solutions.

The experimental results in the removal of metal ions from industrial wastewaters confirm the validity of results obtained in the batch mode studies. However, the percent removal of metal ions from industrial wastewaters by a given concentration of PHC or GAC was lower than that obtained in the aqueous solution. This may be due to other competing ions present in the real wastewaters. The investigation shows that PHC is superior to GAC and can be effectively used for the removal of heavy metal ions from industrial wastewaters.

5.3 Fixed-bed adsorption studies

It is known that the efficiency of a fixed bed system depends on the flow rate, bed height and initial adsorbate concentration. The contact time of adsorbates and adsorbents is the most significant
factor and is short in the fixed bed adsorption process [243]. Therefore experiments were undertaken 
at four different flow rates (Figs.63-72). Examination of these figures show that the low flow rate 
produced better adsorptive effect than a high flow rate. Because the former can increase the contact 
time of the metal bath and the adsorbent, it can allow the metal ions to aggregate on the surface 
and/or to enter into the internal pore structure of the adsorbent and thus increase the amount of metal 
ions adsorbed by the adsorbents.

Adsorbent mass is usually the major concern in the conceptual design of an adsorption system 
and therefore the influence of bed height on the adsorption of metal ions was investigated at four 
different bed heights (Figs.73-82). The results illustrate how much each metal ion can be removed 
using a specific amount of PHC or GAC for 50% breakthrough.

Usually the service time of a fixed bed column system depends greatly on the concentration 
of the solution. Therefore experiments were undertaken at four different initial metal ion 
concentrations at a pH where there was no precipitate formation by hydrolysis for both carbons to 
study the effect of varying the initial metal ion concentration on the rate of removal (Figs.83-92). It is 
evident from the figures that the low metal ion concentration resulted in a longer service time than the 
high initial metal ion concentration for both carbons. Higher initial metal ion concentration saturates 
the adsorbent much faster than lower initial metal ion concentration, hence reducing the service time 
of the column. Adsorbents need a longer time to remove metal ions from more concentrated 
solutions.

Plots for the ratio of effluent concentration to influent concentration \(\left(\frac{C_t}{C_0}\right)\) vs effluent 
volume of various flow rates (Figs.63-72), bed heights (Figs.73-82) and initial metal ion concentrations 
(Figs.83-92) are typical 'sigmoidal shape' and show that increasing the flow rate (Tables 39, 42, 45, 
48 and 51) and initial metal ion concentration (Tables 41, 44, 47, 50 and 53) decreases the 
breakthrough volume and 50% breakthrough time and increasing the bed height (Tables 40, 43, 46, 
49 and 52) increases the breakthrough volume and 50% breakthrough time for Hg(II), Pb(II), Cd(II), 
Ni(II) and Cu(II) for both PHC and GAC. It can be seen that for any metal ion at any flow rate 
(Tables 39, 42, 45, 48 and 51), bed height (Tables 40, 43, 46, 49 and 52) or initial metal ion
concentration (Tables 41, 44, 47, 50 and 53), the breakthrough volumes at \( \frac{C_t}{C_0} = 0 \) and 0.5 and time for 50% breakthrough are greater for PHC than for GAC, even though the initial metal ion concentration used is very much smaller for GAC than for PHC.

A simpler approach to fixed bed adsorber has been proposed by Hutchins [202] to correlate the service time, \( t \) with the process variables. The model is called Bed-Depth-Service-Time (BDST) and is given by the equation (2) or (3). Linear plots of \( C_0t \) vs \( \log_e[(C_0/C_t)-1] \) at different flow rates (Tables 54-63 and Figs.93-102), bed heights (Tables 64-73 and Figs.103-112) and initial metal ion concentrations (Tables 74-83 and Figs.113-122) show that the fixed bed removal of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) obey the BDST model for both PHC and GAC.

The values of \( k_a \) and \( N_0 \) were calculated from the slope and intercept of the plots at different flow rates (Figs.93-102), bed heights (Figs.103-112) and initial metal ion concentrations (Figs.113-122) and are presented in (Tables 84-88; 89-93; and 94-98), respectively. Increasing the flow rate, \( u \) decreased the adsorption capacity, \( N_0 \) and increased the rate constant, \( k_a \) for all the metal ions studied for both carbons. Increasing the bed heights, \( H \) and initial metal ion concentration, \( C_0 \) generally increased the adsorption capacity for all the metal ions studied and decreased the rate constant for both carbons. Generally, for any metal ion, the adsorption rate constant, \( k_a \) of PHC is smaller than that of GAC, while the adsorption capacity, \( N_0 \) of PHC is greater than that of GAC. The adsorption capacity, \( N_0 \) of both carbons for different metal ions from the fixed bed adsorption systems decreased in the order \( \text{Pb(II)} > \text{Hg(II)} > \text{Cu(II)} > \text{Ni(II)} > \text{Cd(II)} \).

5.4 Mechanism of adsorption

The major mechanism of \( M^{2+} \) seems to be ion exchange. A pure carbon surface is considered to be non-polar, but in actual practice some carbon-oxygen complexes (\( C_xO \), \( CO_x \) and \( C_xO_2 \)) are usually present, which render the surface slightly polar. Since there is no satisfactory method for determining the polar character of the surface quantitatively, the above statement is relative [20, 134, 244]. The surface oxygen complexes hydrolyse water molecules as shown below:
\[
C_xO + 2H_2O \rightarrow C_xOH_2^{2+} + 2 OH^- \quad (8)
\]
\[
CO_x + x H_2O \rightarrow (C(OH)_x)^+ + x OH^- \quad (9)
\]
\[
C_xO_2 + H_2O \rightarrow C_xO^{2+} + 2 OH^- \quad (10)
\]

Since PHC was prepared upon treatment with sulphuric acid and sodium bicarbonate, groups such as \(C_xONa^+\), \(C_xONa_2^{2+}\), \(C_xSO_3 H\) and \(C_xSO_3Na\) are also assumed to be present. \(Na^+\) in the above groups are also exchanged with \(H^+\) in the medium as follows:

\[
C_xONa^+ + H^+ \rightarrow C_xOH^+ + Na^+ \quad (11)
\]
\[
C_xONa^+ + 2 H^+ \rightarrow C_xOH_2^{2+} + Na^+ \quad (12)
\]
\[
C_xONa_2^{2+} + 2 H^+ \rightarrow C_xOH_2^{2+} + 2Na^+ \quad (13)
\]
\[
C_xSO_3 Na + H^+ \rightarrow C_xSO_3H + Na^+ \quad (14)
\]

Figures 37, 39, 41, 43 and 45 present the effect of initial pH on final pH at different concentrations of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) for PHC. The curve referred to as blank was obtained under conditions such that \([M(II)] = 0\). Reactions (8) to (14) contribute to an increase in pH in the blank curve. At the same time, reactions (11) to (14) lead to the release of \(Na^+\). Excess \(Na^+\) was introduced into PHC when it was washed with sodium bicarbonate to neutralise any free sulphuric acid during the preparation of PHC (see Table 1). When the metal ion is present in solution, its adsorption will free some \(H^+\) and pH increase will be lower than in the blank (Eqs. 15, 16 and 19).

At the same time, \(Na^+\) will also be released according to reactions (17, 18 and 20).

\[
2 C_xOH^+ + M^{2+} \rightarrow (C_xO)_2M^{2+} + 2H^+ \quad (15)
\]
\[
C_xOH_2^{2+} + M^{2+} \rightarrow C_xOM^{2+} + 2H^+ \quad (16)
\]
\[
2C_xONa^+ + M^{2+} \rightarrow (C_xO)_2M^{2+} + 2Na^+ \quad (17)
\]
\[
C_xONa_2^{2+} + M^{2+} \rightarrow C_xOM^{2+} + 2Na^+ \quad (18)
\]
\[
2C_xSO_3H + M^{2+} \rightarrow (C_xSO_3)_2M + 2H^+ \quad (19)
\]
\[
2C_xSO_3Na + M^{2+} \rightarrow (C_xSO_3)_2M + 2Na^+ \quad (20)
\]
Tests performed by agitating 30 and 50 mg of PHC for 3 h at an initial pH of 4.0 led to a sodium concentration of 18 and 21 mg/L, respectively in the remaining solution. Also, when the concentration of Pb(II) in the solution was increased from 0 to 50 mg/L and of Hg(II), Cd(II), Ni(II) and Cu(II) from 0 to 25 mg/L, the difference between the final pH value of the test containing M(II) and that of blank increased, as expected.

Also, the sodium release increased from 18 to 43 mg/L when the concentration of Pb(II) was increased from 0 to 50 mg/L. Similarly when the concentration of Hg(II), Cd(II), Ni(II) and Cu(II) was increased, from 0 to 25 mg/L, the sodium release increased from 18 to 36 mg/L, 18 to 35 mg/L, 21 to 31 mg/L and 18 to 38 mg/L, respectively. This indicated that apart from exchange of H+ ions on the adsorbent with M2+ ions, significant Na+ ions which were present in the adsorbent were also exchanged with M2+ ions.

Since the details of manufacturing and activation processes for GAC are not known, it is not possible to discuss how Na+ was introduced into GAC. The observations for the effect of initial pH on final pH for GAC were similar to PHC (Figs.38, 40, 42, 44 and 46). Hence it can be said that ion exchange mechanism is important to adsorption processes for both PHC and GAC.

The ion exchange model described above does not satisfactorily explain the sudden increase in adsorption of metal ions over a narrow pH range of 2.0 to 4.0 for both carbons.

In order to describe completely the adsorption reaction of heavy metal ions at the solid-solution interface, an account of all the reactive species in the solution phase is essential. One parameter that controls the extent of hydrolysis of the heavy metal ions is the solution pH. In the adsorption studies of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) described in this thesis, the metal cation exist predominantly as unhydrolysed cation, a condition which was achieved by maintaining the solution pH at values less than $p^*K_1$ (where $K_1$ is the first hydrolysis constant). At the same time the existence of relatively minor amounts of the hydrolysis species, M(OH)+ and M(OH)2-, in equilibrium with the metal ion, M2+, should not be overlooked [245], since they may be more reactive and hence determine adsorption. The $p^*K_1$ values of Hg(II), Pb(II), Cd(II), Ni(II) and
Cu(II) differ significantly, hence the hydrolysis of one cation may be negligible at a pH where a more acidic cation would be extensively hydrolysed.

First hydrolysis constants [245, 246]

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>p*K₁</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg(II)</td>
<td>3.55</td>
</tr>
<tr>
<td>HgCl₂ (aq)</td>
<td>9.56</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>7.80</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>9.00</td>
</tr>
<tr>
<td>Ni(II)</td>
<td>9.86</td>
</tr>
<tr>
<td>Cu(II)</td>
<td>8.00</td>
</tr>
</tbody>
</table>

James and Healy [247] proposed a model in which adsorption is the result of competition between the free energy changes favourable to adsorption, i.e., coulombic (ΔG° coul) and chemical energy changes (ΔG° chem) and the unfavourable change in solvation energy (ΔG° solv):

\[ ΔG°_{ads} = ΔG°_{coul} + ΔG°_{solv} + ΔG°_{chem} \]  \hspace{1cm} (21)

where ΔG°ads denotes the net free energy change for adsorption. The author proposed that a sudden increase in adsorption over a narrow pH range, which coincided with a sudden reversal of the zeta potential, was due to the interfacial precipitation of the hydroxide of the adsorbing metal ion. This precipitation occurred at a pH below that at which it would occur in the bulk solution, because the solubility product at the interface was lowered by the electrostatic field. At higher pH, another charge reversal occurred, which corresponded to the ZPC of adsorbed metal hydroxides. This model was supported by the adsorption of Co(II), La(III), Th(IV) on SiO₂ [247], Co(II) on MnO₂ [248], Zn(II) on MnO₂ [249] and Fe(II) [122], Ni(II) [125], Cd(II) [124] and Pb(II) [123] on 'waste' Fe(III)/Cr(III) hydroxide.
In the James and Healy model [247], the major surface active species are the hydrolysis products in a solution of divalent metal cation (M^{2+}); the species present besides the unhydrolysed M^{2+} ion at pH values less than but close to p^K_{1} include MOH^+, M(OH)^{2-}, M(OH)^{3-} and M(OH)^{4-} although in much smaller amounts. The removal of M(OH)^+ and M(OH)^{2-} species from solution would induce the dominant M^{2+} ion to hydrolyse with the release of one or two H^+ ions for every M(OH)^+ and M(OH)^{2-} species, respectively, adsorbed. These reactions can be represented schematically as follows:

\[
M^{2+} \leftrightarrow M(OH)^+ + H^+ \quad \text{and} \quad M^{2+} \leftrightarrow M(OH)^{2-} + 2H^+
\]

In a model of this type, the uncharged M(OH)^{2-} entity is not subjected to the adverse coulombic and solvation energy terms, which the M^{2+} and M(OH)^+ ions of Hg(II), Pb(II), Cd(II), Ni(II) and Cu(II) would experience if they adsorbed on positively charged PHC and GAC surfaces. Even when the surface is negatively charged an adverse solvation energy exists for positively charged ions which opposes adsorption.

While the coulombic and solvation terms present no barrier to the adsorption of M(OH)^{2-}, neither do they assist the adsorption process. The driving force for adsorption must be found in the chemical free energy term, \( \Delta G_{\text{chem}} \). It is postulated that \( \Delta G_{\text{chem}} \) when favourable to adsorption, indicates short range covalent bonds between hydroxyl groups on the M(OH)^{2-} species (co-ordinated water molecules could not fulfil the same function since they do not have the same ability to donate electrons) and electrophilic centres on the adsorbent surface which is termed as non-electrostatic specific adsorption [181, 214]. A similar argument applies to the adsorption of M(OH)^+ species. However, the molar free energy of adsorption of M(OH)^+ must be less than that for M(OH)^{2-}, since adverse coulombic and solvation, energy terms exist and only one, rather than two
reactive hydroxyl groups is available for bonding to the surface. The heavy metal atoms are considered to be bonded to the surface through two hydroxyl bridges for $M(OH)_2^0$ or one for $M(OH)^+$ and to be attached to two and one surface site, respectively.

In the plots of percent adsorption vs pH (Figs. 27-36), there is a sharp increase in adsorption over a narrow range of pH and this is consistent with the attainment of a pH value at which adsorption of $M(OH)^+$ becomes possible [250] (Equation 23). It was proposed by Davis and Leckie [251] that the most likely forms of the adsorbed ions are $M^{2+}$ and $M(OH)^+$. Hence, the possible adsorption reactions include the following:

\[
\begin{align*}
C_xOH^+ + M^{2+} & \rightarrow C_xOM^{2+} + H^+ & (22) \\
C_xOH^+ + MOH^+ & \rightarrow C_xOMOH^+ + H^+ & (23) \\
2C_xOH^+ + M^{2+} & \rightarrow \text{C}_x\text{O}_2 \text{M}^{2+} + 2H^+ & (24) \\
C_xOH^+ + M^{2+} + H_2O & \rightarrow \text{C}_x\text{O} \text{MOH}^+ + 2H^+ & (25) \\
C_xO + M^{2+} & \rightarrow \text{C}_x\text{OM}^{2+} & (26) \\
C_xO + MOH^+ & \rightarrow \text{C}_x\text{OMOH}^+ & (27)
\end{align*}
\]